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(54) PROCESS FOR PREPARING HIGHLY STEREOREGULAR POLYOLEFINS AND CATALYST USED THEREFOR

(71) We, MITSUI PETROCHEMICAL INDUSTRIES LTD., a Japanese body corporate of 2—5, 3-chome, Kasumigaseki, Chiyoda-ku, Tokyo, Japan, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

This invention relates to a process for polymerizing α -olefins in the presence of a catalyst capable of maintaining its superior catalytic activity for prolonged periods of time thereby to afford in a high yield a highly stereoregular α -olefin polymer or copolymer which has a higher apparent density and a reduced content of halogen ascribable to the catalyst used; and to said catalyst.

Catalyst systems composed of solid titanium halides and organoaluminum compounds have previously been used for preparing highly stereoregular polymers of α -olefins. Polymerizations using these catalyst systems afford highly stereoregular polymers; but the yield of the polymer per unit amount of the titanium catalyst component is still low, and an additional step is required to remove the catalyst residue from the resulting polymer. Recently, some methods, for example, those disclosed in Japanese Laid-Open Patent Publications Nos. 16986/73, 16987/73 and 16988/73, have been proposed to remove the defects of the prior art techniques. These methods attempt to obtain highly stereoregular poly(α -olefins) by polymerizing α -olefins such as propylene using a catalyst comprising a solid component which is obtained by reacting a complex compound formed between a titanium halide and a specific electron donor together with an anhydrous magnesium halide, and the reaction product of a trialkyl aluminum and a specific electron donor. With these methods, however, the stereoregularity of the resulting polymer is still insufficient, and the yield of the polymer per titanium atom is still unsatisfactory. In addition, these methods still suffer from the defect that the yield of the polymer per chlorine atom in the catalyst is low because the co-pulverized product has a low level of titanium content, that the polymerization must be performed with a low slurry concentration because of the low apparent density of the resulting polymer, thus rendering the methods economically disadvantageous, and that the polymerization activity of the catalyst is lost within short periods of time.

French Laid-Open Patent Publication No. 2,113,313 (May 29, 1972) discloses a process for selectively preparing either an atactic polymer as a main product or a stereoregular polymer as a main product. This Patent Publication states that when a Ti catalyst component obtained by contacting a titanium compound with a mixture of an active-type magnesium halide carrier and an anhydrous compound of an element of Groups I to IV, for example, Si is used in the above process preferably in the form supported on a carrier and subsequently modified with an electron donor, a stereoregular polymer is obtained as a main product. This Publication, however, illustrates only SiO_2 as the anhydrous compound of Si. Furthermore, this Publication discloses that ethers, thioethers, amines, phosphines, ketones and esters can be utilized as the electron donors, but do not exemplify any specific compounds that fall within the esters. The isotacticity of the polymer shown by the boiling n-heptane extraction residue in all of the Examples of the above Patent Publication is at most about 70%, and therefore, the process of this patent is far from satisfactory for preparing highly stereoregular

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polymers. On the other hand, the electron donor used in this patent for production of isotactic polymers is only N,N',N'',N'''-tetramethyl ethylene diamine. Moreover, only anhydrous lithium chloride and SiO₂ are specifically used in this patent as the anhydrous compound of an element of Groups I to IV.

We have made investigations with a view to removing the defects of the conventional techniques, and consequently found that a titanium-containing catalyst component composed of an organic complex derived from (i) a magnesium halide, (ii) a specific Si compound, preferably organic Si compound, especially preferably an organopolysiloxane, (iii) an organic carboxylic acid ester and (iv) a specific Ti compound, when combined with an organoaluminum compound, provides a superior catalyst for use in the preparation of highly stereoregular polyolefins. Our investigations also led to the discovery that by using this catalyst, highly stereoregular α -olefin polymers or copolymers can be prepared in high yields while maintaining the superior catalytic activity over a long period of time, and that the halogen content of the resulting polymer or copolymer ascribable to the catalyst can be reduced and the resulting polymers or copolymers have a high apparent density.

The invention accordingly provides a catalyst suitable for use in preparing polymers of α -olefins having at least 3 carbon atoms, the catalyst comprising

(A) a titanium-containing solid catalyst component composed of an organic complex obtained by contacting, in any desired order:

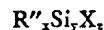
- (i) a magnesium dihalide,
- (ii) a silicon component selected from:
 - (a) compounds of the formula



wherein R'' is alkyl, alkenyl, cycloalkyl or aryl;

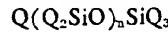
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- (b) compounds of the formula



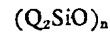
wherein R'' is as hereinbefore defined, X is halogen, x and z are 0 or an integer of at least 1, y is an integer of not less than 2, and x+z=2y+2;

(c) compounds of the formula:



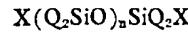
wherein each Q is the same or different, and represents hydrogen, alkyl, cycloalkyl or aryl, with the proviso that the Q groups are not all hydrogen at the same time, and n is an integer of 1 to 1000;

(d) cyclic compounds of the formula:



wherein Q and n are as hereinbefore defined; and

- (e) compounds of the formula:



wherein Q, X and n are as hereinbefore defined;

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- (iii) an organic carboxylic acid ester, and
- (iv) a titanium compound of the formula:



wherein R is alkyl, X is as hereinbefore defined, and l is 0 or an integer of 1 to 4, and

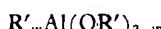
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(B) an organoaluminium catalyst component of the formula:



wherein each R' is the same or different, and represents alkyl, and m is a positive number of 1.5 to 3.

5 The invention also provides a process for preparing olefin polymers which comprise polymerising or copolymerising at least one α -olefin of at least 3 carbon atoms in the presence of a catalyst of the invention.

10 The polymerisation or copolymerisation of α -olefins of at least 3 carbon atoms, as referred to in this application, includes the homopolymerisation of an α -olefin of at least 3 carbon atoms, the copolymerisation of at least two such α -olefins with each other, and the copolymerisation of an α -olefin of at least 3 carbon atoms with ethylene and/or a diolefin, preferably in an amount of up to 30 mol %.

15 Examples of α -olefins which may be polymerised in accordance with the invention are propylene, 1-butene, 4-methyl-1-pentene, and 3-methyl-1-butene, and examples of the diolefins include conjugated diolefins such as butadiene and non-conjugated dienes such as dicyclopentadiene, ethylenenorbornene and 1,5-hexadiene.

20 Examples of component (i) are magnesium chloride, magnesium bromide and magnesium iodide, magnesium chloride ($MgCl_2$) being especially preferred.

25 Preferred examples of component (ii) are compounds of formula (a) or (b) wherein R'' is C_1-C_{18} alkyl, C_3-C_{10} cycloalkyl, preferably C_4-C_6 cycloalkyl, optionally substituted, for example, by C_1-C_4 alkyl, or C_6-C_{14} aryl optionally substituted, for example, by C_1-C_4 alkyl and X when present is chlorine, bromine or iodine, or compounds of formula (c), (d) or (e) wherein each Q group is the same or different, and each represents hydrogen, C_1-C_4 alkyl, C_3-C_8 cycloalkyl or C_6-C_8 aryl and X when present is chlorine, bromine or iodine.

30 Examples of the organic carboxylic acid esters (iii) include esters formed between C_2-C_8 , preferably C_1-C_4 , saturated or C_2-C_8 , preferably C_2-C_4 , unsaturated aliphatic carboxylic acids which may optionally be substituted by halogen and alcohols selected from C_1-C_8 , preferably C_1-C_4 , saturated or C_2-C_8 , preferably C_2-C_4 , unsaturated aliphatic primary alcohols, C_3-C_8 , preferably C_3-C_6 , saturated or unsaturated alicyclic alcohols and C_1-C_4 saturated or C_2-C_4 unsaturated aliphatic primary alcohols substituted by C_6-C_{10} , preferably C_6-C_8 , aromatic groups or halogen esters formed between C_7-C_{12} , preferably C_7-C_{10} , aromatic monocarboxylic acids and alcohols selected from C_1-C_8 , preferably C_1-C_4 , saturated or C_2-C_8 , preferably C_2-C_4 , unsaturated aliphatic primary alcohols, C_3-C_8 , preferably C_3-C_6 , saturated or unsaturated alicyclic alcohols and C_1-C_4 saturated or C_2-C_4 unsaturated aliphatic primary alcohols substituted by C_6-C_{10} , preferably C_6-C_8 , aromatic groups or halogen; and alicyclic carboxylic acid esters such as methyl cyclopentanecarboxylate, methyl hexahydrobenzoate, ethyl hexahydrobenzoate, methyl hexahydrotoluene, and ethyl hexahydrotoluene.

35 In the present invention, a part or the whole of the organic carboxylic acid ester (iii) can be used in the form of ester-treated products or adducts of the compounds (i), (ii) and (iv) by bringing it in advance into contact with these compounds (i), (ii) and (iv).

40 Desirably, the magnesium halide (i) as a constituent of the titanium-containing solid catalyst component (A) is as dry as possible, but the inclusion of moisture is permissible to an extent such that the moisture does not substantially affect the performance of the catalyst. The halide may be one obtained by dehydrating a commercially available grade at 100 to 400°C. under reduced pressure prior to use. For convenience of use, the magnesium halide is preferably used in the form of a powder having an average particle diameter of 1 to 50 microns. But when it is to be pulverized by a mechanical contacting treatment during catalyst preparation, powders of larger particle sizes can also be used. The average particle diameter of 1 to 50 microns mean that at least 80% by weight of the total particles have a particle diameter of 1 to 50 microns.

45 Specific examples of the compounds of the formula R''_4Si for use as component (ii)(a) include tetraalkyl silanes such as tetramethyl silane, tetraethyl silane, tetra-n-propyl silane, tetra-n-butyl silane and tetra(n- or i-) amyl silane, tetraaryl silanes such as tetraphenyl silane or tetra(3- or 4-) tolyl silane, and tetracycloalkyl silanes such as tetracyclopentyl silane, tetracyclohexyl silane or tetrakis (3- or 4-) methylcyclohexyl silane.

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Specific examples of the compounds of $R''_x Si_x X_z$ for use as component (ii)(b) include the following.

[I] Where $x=0$, and $y=2$, the compounds are expressed by the following general formula



wherein $z=2y+2$, and y is usually an integer of 2 to 10.

Examples are polyhalopolysilanes such as hexahalodisilanes, octahalotrisilanes, decahalotetrasilanes, dodecahalopentasilanes, tetradecahalohexasilanes or docosahalo-decasilanes. In these polyhalopolysilanes, the halogen atoms may be identical or different. Specific examples include trichlorotribromodisilane, hexachlorodisilane, hexabromodisilane, hexaiododisilane, hexafluorodisilane, octachlorotrisilane, octabromo-trisilane, decachlorotetrasilane, dodecachloropentasilane, and docosachlorodecasilane. Of these, the hexachlorodisilane, hexabromodisilane, and trichlorotribromodisilane are preferred.

[II] Where $x=1$ and $y=2$, the compounds are expressed by the general formula $R''_x Si_x X_z$, in which $x+z=2y+2$, and y is usually an integer of 2 to 8.

Specific examples of these compounds are as follows:

(a) Where $x=1$ and $y=2$:

Methylpentachlorodisilane, ethylpentachlorodisilane, 1,1 - dimethyl - 1,2,2,2-tetrachlorodisilane, 1,1 - diethyl - 1,2,2,2 - tetrachlorodisilane, 1,1,2 - trimethyl-1,2,2 - trichlorodisilane, 1,1,1 - trimethyl - 2,2,2 - trichlorodisilane, 1,1,2 - tri - i-butyl - 1,2,2 - trichlorodisilane, 1,1,2,2 - tetramethyl - 1,2 - dichlorodisilane, 1,1,1,2-tetramethyl - 2,2 - dichlorodisilane, pentamethylchlorodisilane, 1 - chloromethyl-1,1,2,2 - tetramethyl - 2 - chlorodisilane, penta - n - butylchlorodisilane, hexamethyl-disilane, hexa - n - propyldisilane, hexa - n - butyldisilane, phenylpentachlorodisilane, 4 - tolylpentachlorodisilane, 1,1 - diphenyl - 1,2,2,2 - tetrachlorodisilane, 1,1,2 - triphenyl - 1,2,2 - trichlorodisilane, 1,1,1 - triphenyl - 2,2,2 - trichlorodisilane, 1,1,2,2 - tetraphenyl - 1,2 - dichlorodisilane, pentaphenylchlorodisilane, penta(1 - naphthyl)chlorodisilane, hexaphenyldisilane, sym - tetramethyl - diphenyl-disilane, 1,1,1,2 - tetramethyl - 2 - phenyl - 2 - chlorodisilane, and tetracyclohexyl-disilane.

(b) Where $1 \leq x \leq 8$ and $y=3$, the compounds are expressed by $R''_x Si_x X_{z-x}$ in which x is an integer of not more than 8.

Specific examples of these compounds are as follows:

[In paragraphs (b), (g), (d) and (e), Me stands for a methyl group; Et, an ethyl group; Ph, a phenyl group; and Bu, a butyl group.]

$(SiMe_2Cl)_2Si(Me)Cl$, $(SiMe_2Cl)_2SiMe_2$,
 $(SiMe_3)_2SiCl_2$, $(SiMe_3)_2Si(Me)Cl$, $(SiMe_3)_2SiMe_2$,
 $SiMe_2$, $(SiMe_3)_2SiPh_2$, $(SiPh_3)_2SiMe_2$,
 $Me(SiMe_2)_3Cl$, $Me(SiMe_2)_3Br$, $Me(SiMe_2)_3$,
 Me , $C_6H_5(SiMe_2)_3Me$, $Ph(SiMe_2)_3Ph$, and
 $Ph(SiPh_2)_3Ph$.

[g] Where $x=2$ and $y=4$, the compounds are expressed by the general formula $R''_x Si_x X_{10-x}$ wherein x is an integer of not more than 10.

Examples of these compounds are as follows:

$Cl(SiMe_2)_4Cl$, $Cl(SiMe_2)_4Ph$,
 $Me(SiMe_2)_4Me$, $Et(SiMe_2)_4Et$,
 $Ph(SiMe_2)_4Ph$, $Ph(SiPh_2)_4Ph$,
 $Me(SiPh_2)_4Me$, $(Me_3Si)_3SiCl$,
 $(PhMe_2Si)_3SiCl$, $(Me_3Si)_3SiMe$, and
 $(Me_3Si)_3SiPh$.

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(d) Where $x=2$ and $y=5$, the compounds are expressed by the general formula $R''_x Si_x X_{12-x}$ wherein x is an integer of not more than 12.

Examples of these compounds are as follows:

5 $Cl(Me_2Si)_5 Cl$, $Me(Me_2Si)_5 Cl$,
 $Ph(Me_2Si)_5 Cl$, $Cl(Ph_2Si)_5 Cl$,
 $Me(Me_2Si)_5 Me$, $Ph(Me_2Si)_5 Ph$,
 $(Me_2ClSi)_4 Si$, $(Me_3Si)_4 Si$,
 $Me_3Si(Pb_2Si)_4 SiMe_3$, and
 $Ph_3Si(Ph_2Si)_3 SiPh_3$.

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(e) Where $x=2$ and $y=6$, the compounds are expressed by the general formula $R''_x Si_x X_{14-x}$ wherein x is an integer of not more than 14.

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Examples of these compounds are as follows:

15 $Cl(Me_2Si)_6 Cl$, $Me(Me_2Si)_6 Cl$,
 $Ph(Me_2Si)_6 Cl$, $Me(Me_2Si)_6 Me$,
 $Ph(Me_2Si)_6 Ph$, $Me(Ph_2Si)_6 Me$,
 $Me_3Si(Me_2Si)_4 SiMe_3$, $Ph_3Si(Me_2Si)_4 SiPh_3$, and
 $Me_3Si(Ph_2Si)_4 SiMe_3$.

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20 Specific examples of linear polysiloxanes of the formula $Q(Q_2SiO)_n SiQ_3$ for use as the Si component (ii)(c) are hexamethyldisiloxane, decamethyltetrasiloxane, tetracosamethylundecasiloxane, 3-hydroheptamethyltrisiloxane, 3,5-dihydrooctamethyltetrasiloxane, 3,5,7-trihydrononamethylpentasiloxane, tetramethyl-1,3-diphenyldisiloxane, pentamethyl-1,3,5-triphenyltrisiloxane, heptaphenyldisiloxane, and octophenyltrisiloxane.

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25 Specific examples of cyclopolysiloxanes of the formula $(Q_2SiO)_n$ for use as the Si component (ii)(d) include 2,4,6-trimethylcyclotrisiloxane, 2,4,6,8-tetramethylcyclo-tetrasiloxane, hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane, decamethyl-cyclopentasiloxane, dodecamethylcyclohexasiloxane, triphenyl-1,3,5-trimethylcyclotri-siloxane, hexaphenylcyclotrisiloxane, and octaphenylcyclotetrasiloxane.

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30 Specific examples of linear α,ω -dihalopolysiloxanes of the formula

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$X(Q_2SiO)_n SiQ_2X$

for use as the Si component (ii)(e) include 1,3-dichlorotetramethyldisiloxane, 1,5-dichlorohexamethyltrisiloxane, and 1,7-dichlorooctamethyltetrasiloxane.

35 Of these organic polysiloxanes, the linear alkylpolysiloxanes are preferred. Methyl-polysiloxane and ethylpolysiloxane having a viscosity of not more than 200 centipoises at 25°C. are especially preferred.

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Specific examples of the organic carboxylic acid ester as component (iii) of the titanium-containing solid catalyst component (A) are primary alkyl esters of monovalent saturated fatty acids such as methyl formate, ethyl acetate, n-amyl acetate, 2-ethylhexyl acetate, n-butyl formate, ethyl butyrate, or ethyl valerate; benzyl acetate; allyl acetate; primary alkyl esters of haloaliphatic carboxylic acids such as ethyl chloroacetate, n-propyl dichloroacetate and ethyl chlorobutyrate; primary alkyl esters of unsaturated fatty acids such as methyl acrylate, methyl methacrylate or i-butyl crotonate; primary alkyl esters of benzoic acid such as methyl benzoate, ethyl benzoate, n-propyl benzoate, n- and i-butyl benzoates, n- and i-amyl benzoates, n-hexyl benzoate, n-octyl benzoate and 2-ethylhexyl benzoate; primary alkyl esters of toluic acid such as methyl toluate, ethyl toluate, n-propyl toluate, n- and i-butyl toluates, n- and i-amyl toluates or 2-ethylhexyl toluate; primary alkyl esters of ethylbenzoic acid such as methyl ethylbenzoate, ethyl ethylbenzoate, n-propyl ethylbenzoate, and n- and i-butyl ethylbenzoates; primary alkyl esters of xylylenecarboxylic acid such as methyl 3,4-xylylene-1-carboxylate, ethyl 3,5-xylylene-1-carboxylate, and n-propyl 2,4-xylylene-1-carboxylate; primary alkyl esters of anisic acid such as methyl anisate, ethyl anisate, n-propyl anisate, and n- and i-butyl anisates; and primary alkyl esters of naphthoic acid such as methyl naphthoate, ethyl naphthoate, n-propyl naphthoate, and n- and i-butyl naphthoates.

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45 Of these primary alkyl esters of aromatic carboxylic acids, primary C₁—C₄ alkyl esters are preferred. Methyl benzoate and ethyl benzoate are especially preferred.

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As already mentioned, a part or the whole of the organic carboxylic acid ester (iii) can be used in the form of ester-treated products or adducts of the compounds (i), (ii) and (iv) by bringing it in advance into contact with these compounds (i), (ii) and (iv).

Specific examples of the titanium compound of formula $Ti(OR)_2X_{4-i}$ [component (iv)] include titanium tetrahalides such as titanium tetrachloride, titanium tetrabromide or titanium tetraiodide; alkoxy titanium trihalides such as methoxy titanium trichloride, ethoxy titanium trichloride, n-butoxy titanium trichloride, ethoxy titanium tribromide or i-butoxy titanium tribromide; dialkoxy titanium dihalides such as dimethoxy titanium dichloride, diethoxy titanium dichloride, di-n-butoxy titanium dichloride or diethoxy titanium dibromide; trialkoxy titanium monohalides such as trimethoxy titanium chloride, triethoxy titanium chloride, tri-n-butoxy titanium chloride and triethoxy titanium bromide; and tetraalkoxy titanums such as tetramethoxy titanium, tetraethoxy titanium and tetra-n-butoxy titanium. Of these, the titanium tetrahalides, especially titanium tetrachloride, are preferred.

When a magnesium halide (i) treated with the organic carboxylic acid ester (iii) is used in the formation of the titanium-containing solid catalyst component (A) used in this invention, it is preferred to use a mechanical pulverizing means for contacting both with each other. According to this pulverizing contact, the organic acid ester in a wide range of proportions acts effectively on the magnesium halide. A sufficient treating effect can be obtained even if the proportion of the former is small as compared with the latter (in a molar ratio of 1/1 to 1/20).

When the Si component (ii) treated with the organic carboxylic acid ester (iii) is used, the treatment is effected, for example, by a method comprising adding the organic carboxylic acid ester at room temperature to a silicon compound itself or its solution in a suitable inert solvent such as pentane, hexane, heptane or kerosene, or a method comprising preparing a solution of the organic carboxylic acid ester in the above inert solvent, and then adding the silicon compound to the solution. Of course, the treatment can be completed within short periods of time at an elevated temperature, but if desired, the treatment can also be carried out under cooling.

When the titanium compound (iv) is used in the form of an adduct of it with the organic carboxylic acid ester (iii), the adduct can be prepared by adding the organic carboxylic acid ester (iii) in an equimolar or larger amount (calculated based on the ester) to the titanium compound itself (if it is liquid) or a solution of it in the above inert solvent (if it is solid), and separating the resulting precipitate by filtration. Even when the titanium compound is liquid, it can be used in the adduct-forming reaction in the form of its solution in the above inert solvent. The washing of the resulting precipitate (the removal of the unreacted titanium compound and organic carboxylic acid ester) can also be carried out using the above solvent.

The ratio of the anhydrous magnesium halide (i)/the Si component (ii)/the organic carboxylic acid ester (iii)/the titanium compound (iv) as the starting materials for the catalyst component (A) is not particularly restricted, but is usually 1/1000—0.01/10—0.005/100—0.001, preferably 1/10—0.01/1—0.01/30—0.01.

Preferably, the titanium-containing solid catalyst component (A) is prepared by bringing the components (i), (ii), (iii) and (iv) into contact with each other under pulverizing conditions. A number of modes are possible in regard to the order of addition of these components, the method of addition and the method of contacting, and some examples are described below:

(1) The anhydrous magnesium halide (i), the Si component (ii), the organic carboxylic acid ester (iii) and the titanium compound (iv) are contacted with each other intimately by a mechanical pulverizing means (to be referred to as pulverizing contact), and the resulting titanium-containing solid component is treated preferably with the compound (iv) or its solution in an inert solvent;

(2) The magnesium halide (i), the Si component (ii), and the organic carboxylic acid ester are pulverizingly contacted. The resulting solid component is treated by suspending in the titanium compound (iv) or its solution in an inert solvent. Or the solid component and the titanium compound (iv) are pulverizingly contacted in the substantially dry state, and then treated by suspending preferably in the titanium compound (iv) or its solution in an inert solvent;

(3) The anhydrous magnesium halide (i) and the organic carboxylic acid ester (iii) are pulverizingly contacted and then further contacted pulverizingly with the Si component (ii) to form a solid component. Or the magnesium halide (i) and the Si component (ii) are first pulverizingly contacted and then with the organic carboxylic acid ester (iii) to form a solid component. Either of such solid components is suspended in the titanium compound (iv) or its solution in an inert solvent to

treat it. Or the solid component is pulverizingly contacted with the titanium component (iv) substantially in the dry state, and then suspended preferably in the titanium compound (iv) or its solution in an inert solvent to treat it;

(4) The anhydrous magnesium halide (i), the Si component (ii) and an adduct of the titanium compound (iv) and the organic carboxylic acid ester (iii) are pulverizingly contacted, and the resulting titanium-containing solid component is suspended preferably in the titanium compound (iv) or its solution in an inert solvent to treat it;

(5) The anhydrous magnesium halide (i) and the Si component (ii) are pulverizingly contacted, and then further pulverizingly contacted with an adduct of the titanium compound (iv) and the organic carboxylic acid ester (iii). The resulting titanium-containing solid component is suspended preferably in the titanium compound (iv) or its solution in an inert solvent to treat it;

(6) In the procedures of (1) and (3) above, the titanium compound (iv) is used in the form of an adduct of it with the organic carboxylic acid ester (iii).

(7) The anhydrous magnesium halide (i), the Si component (ii), the titanium compound (iv), and an adduct of the titanium compound (iv) and the organic carboxylic acid ester (iii) are pulverizingly contacted, and the resulting titanium-containing solid component is suspended preferably in the titanium compound (iv) or its solution in an inert solvent to treat it; and

(8) In the procedure of paragraph (7) above, the organic carboxylic acid ester (iii) itself is also added to the pulverizing contact system.

The pulverizing contact means in the preparation of the titanium-containing solid titanium component (A) in the present invention may, for example, include means using a rotary ball mill, a vibratory ball mill, or an impact mill. As a result of contact by such a pulverizing contact means, the organic carboxylic acid ester (iii), the Si component (ii) and the titanium compound (iv) immediately act on the active surface resulting from the pulverization of the magnesium halide (i) to form an organic complex whose chemical structure has not been elucidated yet. This can be confirmed by the fact that the diffraction pattern of the magnesium halide powder changes.

The treating conditions employed for pulverizingly contacting two or more of the starting material for the catalyst component (A) using various mills can be selected as follows:

Taking up the use of a rotary ball mill as an example, 100 balls each with a diameter of 15 mm made of stainless steel (SUS 32) were accommodated in a ball cylindrical receptacle made of stainless steel (SUS 32) and having an inner capacity of 800 ml. and an inside diameter of 100 mm. When 20 to 40 g of the materials are placed in it, the pulverization treatment is carried out usually for at least 48 hours, preferably at least 72 hours at a speed of 125 rpm. The temperature for the pulverization treatment is usually a point in the vicinity of room temperature. When there is a marked exotherm, the system is preferably cooled, and the pulverizing contact is performed at a temperature lower than room temperature.

The treatment of the solid component obtained by pulverizing contact of the starting materials of the solid component (A) with the titanium compound (iv) can be suitably carried out by stirring the mixture usually at 40°C. to the boiling point of the treating mixture for at least 1 hour. Alternatively, this can be accomplished by pulverizing contact under the above pulverization conditions for at least 100 hours using the ball mill.

When titanium compounds are used on two different occasions in the above treatment procedure, they may be the same as, or different from, each other so long as they are chosen from compounds of the above general formula.

The titanium-containing solid catalyst component (A) results after separating the organic complex solid prepared in the above manner from the suspension. Preferably, it is fully washed with hexane or other inert liquid media so that the free titanium compound (iv) is no longer detected in the wash liquid.

The catalyst component (B) to be combined with the catalyst component (A) in the present invention is an organoaluminum compound of the general formula $R'_mAl(OR')_{3-m}$ wherein R' is an alkyl group, preferably a C_1-C_4 straight-chain or branched-chain alkyl group, the two or more R' groups being identical or different, and m is a number in the range of $1.5 \leq m \leq 3$.

Examples of the organoaluminum compound are as follows:

(1) When m is 3, the compound is a trialkyl aluminum. Specific examples are trimethyl aluminum, triethyl aluminum, tri-n- and -i-propyl aluminums, tri-n- and -i-butyl aluminum, and trihexyl aluminum. The triethyl aluminum and tributyl aluminum are preferred. They may also be used in combination of two or more.

If desired, the trialkyl aluminum may be reacted with an organic carboxylic acid ester, which may be the same ester or a different ester from that used in preparing the catalyst component (A), prior to use. (Any amount of ester used in this way is additional to the amount of ester (iii) used in preparing the catalyst component (A).) This reaction may be carried out in the polymerization system before the initiation of polymerization; or it may be carried out separately, and then the reaction product is added to the polymerization system. The reaction proceeds sufficiently by contacting the trialkyl aluminum directly with an organic carboxylic acid ester (or using one of them as a solution in an inert solvent). The ratio between the amounts of these materials is such that the proportion of the trialkyl aluminum is usually 2 to 100 mols (based on the aluminum atom) per gram equivalent of the ester group of the organic carboxylic acid ester. The organic carboxylic acid ester may be selected from the various organic carboxylic acid ester as component (iii) in the formation of the catalyst component (A). Usually, it may be the same kind of acid ester as that used in forming the catalyst component (A).

(2) When m is at least 1.5 but below 3 ($1.5 \leq m < 3$), the above aluminum compound is a partially alkoxyated alkyl aluminum. Such an alkyl aluminum is prepared, for example, by adding a calculated amount of an alcohol to a trialkyl aluminum or dialkyl aluminum hydride. Since this reaction is vigorous, at least one of them is preferably used as a solution in an inert solvent in order to cause the reaction to proceed mildly.

In order to polymerize or copolymerize α -olefins having at least 3 carbon atoms using the catalyst composed of the titanium-containing solid catalyst component (A) and the organoaluminum catalyst component (B), polymerization conditions known to be employed in polymerizations or copolymerizations of α -olefins using Ziegler-type catalysts can be properly chosen. Usually, polymerization temperatures of from room temperature to about 200°C. and pressures from atmospheric pressure to about 50 Kg/cm² can be used. The polymerizations or copolymerizations can be carried out either in the presence or in the absence of an inert liquid medium. Examples of the liquid medium are pentane, hexane, heptane, iso-octane and kerosene. Where the polymerization or copolymerization is carried out in the absence of a liquid medium, it may be performed in the presence of a liquid olefin monomer, if it may be carried out in the vapor phase, for example, by using a fluidized bed catalyst.

The concentration of the catalyst to be charged into the polymerization system for polymerization can be changed as desired. For example, in liquid-phase polymerizations, the titanium-containing solid catalyst component (A) is used in a concentration of usually 0.0001 to 1.0 m-mol/liter calculated as titanium atom; and the catalyst component (B) is used in a concentration of usually 1/1 to 100/1, preferably 1/1 to 30/1, in terms of the aluminum atom/titanium atom ratio. In vapor-phase polymerizations, the titanium-containing solid catalyst component (A) can be used in a concentration of 0.001—0.5 m-mol (calculated as titanium atom), and the catalyst component (B), in an amount of 0.01—5 m-mol (calculated as aluminum atom), both per liter of the volume of the reaction zone.

In order to lower the molecular weight of the resulting polymer (in order to increase the melt index of the polymer), hydrogen may be caused to be present in the polymerization system.

The following Examples and Comparative Examples illustrate the present invention more specifically.

Example 1.

Preparation of Catalyst Component (A):—

A 800 ml. stainless steel (SUS 32) ball mill with an inside diameter of 100 mm accommodating therein 100 stainless steel (SUS 32) balls each with a diameter of 15 mm was charged with 20 g of anhydrous magnesium chloride, 6.0 ml. of ethyl benzoate and 3.0 ml. of methyl polysiloxane (having a viscosity of 20 centipoises at 25°C.) in an atmosphere of nitrogen, and pulverizingly contacted for 100 hours at a rotating speed of 125 rpm. The resulting solid product was suspended in 150 ml. of titanium tetrachloride, and the suspension was stirred at 80°C. for 2 hours. Then, the solid component was collected by filtration, and washed with purified hexane until free titanium tetrachloride was no longer detected. The resulting component contained 4.1% by weight of titanium and 58.2% by weight of chlorine as atoms.

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Polymerization:—

A 2-liter autoclave was charged with 0.05 ml. (0.375 m-mol) of triethyl aluminum, 43.8 mg (0.0375 m-mol calculated as titanium atom) of the titanium-containing solid

component (A) obtained above and 750 ml. of kerosene (purified kerosene) sufficiently free from oxygen and moisture. The polymerization system was heated, and when the temperature reached 70°C., propylene was introduced. Polymerization of the propylene was started at a total pressure of 7.0 Kg/cm². After continuing the polymerization at 70°C. for 3 hours, the introduction of propylene was stopped. The inside of the autoclave was cooled to room temperature, and the catalyst was decomposed by addition of methanol. The solid component was collected by filtration, washed with methanol, and dried to afford 410.3 g of polypropylene as a white powder. The boiling n-heptane extraction residue (II) of the powder was 94.5%, and its apparent density was 0.30 g/ml.

On the other hand, concentration of the liquid phase afforded 15.1 g of a solvent-soluble polymer.

The average specific polymerization activity per titanium atom of the catalyst used above was 540 g/Ti-m M . hr . tam.

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Comparative Example 1.

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Preparation of a titanium-containing catalyst component:—

A ball mill of the same type as used in Example 1 was charged with 20 g of anhydrous magnesium chloride and 17.8 g of an adduct having the average composition of the formula $TiCl_4 \cdot C_6H_5COOC_2H_5$, and they were contacted pulverizingly under the same conditions as in Example 1 for 100 hours at a speed of 125 rpm. The resulting solid titanium catalyst component (corresponding to the component (A) in Example 1) was considerably agglomerated in a ball mill, and was difficult to obtain in powder form. A part of the solid component was washed with 1 liter of purified hexane to the same extent as in Example 1, and dried to form a titanium catalyst component. The titanium catalyst component contained 4.2% by weight of titanium and 6.30% by weight of chlorine calculated as atoms.

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Polymerization:—

Propylene was polymerized under the same conditions as in Example 1 using 114 mg of the titanium catalyst component obtained above. There were only obtained 8.8 g of polypropylene as a white powder and 1.7 g of a solvent-soluble polymer.

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Examples 2, 3, 4 and 5.

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In each run, a titanium catalyst component (A) was prepared in the same way as in Example 1 except that each of the polysiloxanes described in Table 1 was used. Propylene was polymerized under the same conditions as in Example 1 using the resulting titanium catalyst component in the amount indicated in Table 1. The results are also shown in Table 1.

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TABLE I
Results of Polymerization

Examples	Catalyst Component		Amount of powdery polymer (g)	Amount of soluble polymer (g)	Extraction residue of the powdery polymer (%)	Apparent density (g/ml.)	Average specific activity*
	Organic Polysiloxane (amount in ml.)	(A) Contents of Ti and Cl (wt. %)					
2	Methylhydropoly-siloxane (3)	40.4	58.0	330	18.0	93.9	0.29
3	Hexamethyldisiloxane (3)	37.4	59.5	395	17.6	93.5	0.28
4	1,3-Dichlorotetramethyl-disiloxane (3)	37.8	59.4	386	19.0	94.4	0.29
5	3-Hydroheptamethyl-tri-siloxane (3)	30.2	61.2	375	15.1	93.9	0.29

* grams of polypropylene/Ti-mmol·hr·atm.

Examples 6 to 8.

In each run, a catalyst component (A) was prepared under the same conditions as in Example 1 except that each of the substituted benzoic acid esters shown in Table 2 was used in the amount shown in Table 2. Propylene was polymerized in the same way as in Example 1 using the catalyst component (A) in the amount shown in Table 2. The results are shown in Table 2.

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TABLE 2

Examples	Organic acid ester (amount in ml.)	Catalyst Component (A)		Results of Polymerization			
		Ti and Cl contents (wt. %)	Cl (wt. %)	Amount used (mg)	Yield of Polymer (g)	Extraction residue of powdery polymer (%)	Apparent density (g./ml.)
6	n-Butyl benzoate (7.48)	4.50	54.6	39.9	401	19.2	0.28
7	Methyl benzoate (7.43)	4.03	59.0	44.6	425	14.1	0.29
8	Ethyl chloroacetate (7.43)	3.64	59.2	49.3	410	25.0	0.28

* Same as the footnote to Table 1.

Example 9.

Preparation of Catalyst Component (A):—

A solid component was prepared by the ball mill treatment of anhydrous magnesium chloride, ethyl benzoate and methylhydropolysiloxane in the same way as in Example 1. The resulting solid component was suspended in 100 ml. of kerosene containing 50 ml. of titanium tetrachloride, and thus treated at 100°C. for 2 hours with stirring. The solid component was collected by filtration, and washed with purified hexane until free titanium tetrachloride was no longer detected. The resulting catalyst component (A) contained 3.0% by weight of titanium and 61.2% by weight of chlorine calculated as atoms.

Polymerization:—

A 2-liter autoclave was charged with 750 ml. of purified kerosene, 0.095 ml. (0.375 m-mol) of triisobutyl aluminum and 59.5 ml. (0.0375 m-mol calculated as titanium atom) of the catalyst component (A). The polymerization system was heated and when the temperature reached 70°C., propylene was introduced. The polymerization of propylene was started at a total pressure of 7.0 Kg/cm². With stirring, the

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polymerization was carried out for 5 hours at 70°C, with stirring, and then the introduction of propylene was stopped. The inside of the autoclave was cooled to room temperature, and the solid component was collected by filtration, washed with methanol and dried to afford 390.4 g of polypolyene as a white powder and 12.1 g of a solvent-soluble polymer. The powdery polymer had an n-heptane extraction residue of 96.4%, and an apparent density of 0.31 g/ml. The average specific polymerization activity of the catalyst was 306 g of polypolyene/Ti-mmol . hr . atm.

Examples 10 to 12. Propylene was polymerized in the same way as in Example 1 except that each 10 of the silicon compounds shown in Table 3 was used instead of the methyl polysiloxane. (The amount of the catalyst component (A) during the polymerization was 0.0375 m-mol calculated as titanium atom which was the same amount as in Example 1.) The results are shown in Table 3.

TABLE 3

Examples	Silicon compound (amount in ml.)	Catalyst Component (A)		Results of Polymerization			
		Ti	Cl	Powdery polymer (g)	Soluble polymer (g)	Extraction residue (%) of powdery polymer	Apparent density (g/ml.)
10	Dimethyl diallyl silane (3.0)	3.05	58.0	156.5	12.8	91.1	0.29
11	Hexachlorodisilane (3.0)	3.12	59.4	161.0	12.3	91.7	0.30
12	Methyl pentachloro- disilane (3.0)	3.08	62.3	138.9	10.7	91.8	0.29

* Same as the footnote to Table 1.

In each run, a catalyst component (A) was prepared under the same conditions as in Example 1 except that each of the polysiloxanes shown in Table 4 was used instead of the methyl polysiloxane. Propylene was polymerized in the same way as in Example 1 using the catalyst component (A) in the amount shown in Table 4. The results are shown in Table 4.

TABLE 4

Examples	Catalyst Component (A) Organic polysiloxane (amount in ml.)	Results of Polymerization				Average specific activity *		
		Ti and Cl contents (wt. %)	Cl (wt. %)	Yield of polymer (g) Powdery polymer	Soluble polymer			
13	Octaphenyl trisiloxane (3)	3.35	59.7	282.6	16.7	93.4	0.29	380
14	2,4,6-Trimethyl cyclotrisiloxane (3)	3.43	60.2	291.1	16.0	94.0	0.29	390
15	Octamethyl cyclotetra- siloxane (3)	3.55	59.5	298.8	18.6	93.8	0.28	403
16	Decamethylcyclopenta- siloxane (3)	3.00	61.0	292.5	15.7	93.7	0.29	366
17	Octaphenyl cyclotetra- siloxane (3)	3.04	60.0	280.7	13.8	93.9	0.28	374

* Same as the footnote to Table 1.

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WHAT WE CLAIM IS:—

1. A catalyst suitable for use in preparing polymers of α -olefins having at least 3 carbon atoms, the catalyst comprising:

5 (A) a titanium-containing solid catalyst component composed of an organic complex obtained by contacting, in any desired order:

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- (i) a magnesium dihalide,
- (ii) a silicon component selected from:

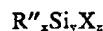
(a) compounds of the formula



10 wherein R'' is alkyl, alkenyl, cycloalkyl or aryl;

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(b) compounds of the formula



wherein R'' is as hereinbefore defined, X is halogen, x and z are 0 or an integer of at least 1, y is an integer of not less than 2, and $x+z=2y+2$;

15 (c) compounds of the formula:

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wherein each Q is the same or different, and represents hydrogen, alkyl, cycloalkyl or aryl, with the proviso that the Q groups are not all hydrogen at the same time, and n is an integer of 1 to 1000;

20 (d) cyclic compounds of the formula:

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wherein Q and n are as hereinbefore defined; and

(e) compounds of the formula:



25 (iii) an organic carboxylic acid ester, and
(iv) a titanium compound of the formula:

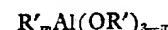
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wherein R is alkyl, X is as hereinbefore defined, and l is 0 or an integer of 1 to 4, and

30 (B) an organoaluminium catalyst component of the formula:

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wherein each R' is the same or different, and represents alkyl, and m is a positive number of 1.5 to 3.

35 2. A catalyst according to claim 1 wherein the magnesium dihalide (i) is magnesium chloride, magnesium bromide or magnesium iodide.

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3. A catalyst according to claim 1 or 2 wherein the silicon component (ii) is a compound (a) or (b) wherein R'' is C_1-C_{11} alkyl, C_8-C_{10} cycloalkyl optionally substituted by C_1-C_4 alkyl, or C_6-C_{14} aryl optionally substituted by C_1-C_4 alkyl and X when present is chlorine, bromine or iodine, or is a compound (c), (d) or (e) wherein each Q is the same or different and represents hydrogen, C_1-C_4 alkyl, C_3-C_6 cycloalkyl or C_6-C_{14} aryl, with the proviso that all Q groups are not all hydrogen at the same time and X when present is chlorine, bromine or iodine.

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4. A catalyst according to claim 1, 2 or 3 wherein the organic carboxylic acid

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ester (iii) is an organic carboxylic acid ester selected from esters formed between a C₁—C_n saturated or unsaturated aliphatic carboxylic acid optionally substituted by halogen and a C₁—C_n saturated or C₂—C_n unsaturated aliphatic primary alcohol, C₃—C_n saturated or unsaturated alicyclic alcohol or saturated or unsaturated aliphatic primary alcohol substituted by at least one C₆—C₈ aromatic group or halogen atom; esters formed between a C₆—C₁₂ aromatic monocarboxylic acid and a C₁—C_n saturated or C₂—C_n unsaturated aliphatic primary alcohol, C₃—C_n saturated or unsaturated alicyclic alcohol or saturated or unsaturated aliphatic primary alcohol substituted by at least one C₆—C₈ aromatic group or halogen atom; and alicyclic carboxylic acid esters selected from methyl cyclopentanecarboxylate, methyl hexahydrobenzoate, methyl hexahydrotoluuate and ethyl hexahydrotoluuate.

5 5. A catalyst according to claim 1 substantially as described in any one of the Examples.

10 6. A process for preparing olefin polymers which comprises polymerising or copolymerising at least one α -olefin of at least 3 carbon atoms in the presence of a catalyst as claimed in any one of the preceding claims.

15 7. A process according to claim 6 wherein the amount of the catalyst is such that the proportion of the titanium-containing solid catalyst component (A) is 0.0001 to 1.0 m-mol/liter, calculated as titanium atom, based on the volume of the liquid phase of the polymerisation system, and the proportion of the organoaluminium catalyst component (B) is 1:1 to 100:1 in terms of the ratio of aluminium atom to titanium atoms.

20 8. A process according to claim 6 wherein the amount of the catalyst is such that the concentration of the catalyst component (A) is 0.001 to 0.5 m-mol (calculated as titanium atom) and of the catalyst component (B) is 0.01 to 5 m-mol (calculated as aluminium atom), both per liter of the volume of the reaction zone.

25 9. A process according to claim 6 substantially as described in any one of the Examples.

30 10. Olefin polymers when prepared by a process as claimed in any one of claims 6 to 9.

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